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Origins and processes of salinization of a Plio-Quaternary coastal Mediterranean multilayer aquifer: the Roussillon Basin case study

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Abstract

Salinization of coastal aquifers represents a threat to groundwater resources, especially in Mediterranean regions. We report geochemical and isotopic vertical variability in the Quaternary and Pliocene aquifer of the Roussillon Basin (S France). Aquifers layers are not equally impacted by salinization, with EC ranging from 459 to 43000 µS.cm^{-1}. Groundwater chemical compositions highlight cation exchange processes, in addition to a simple binary mixing between fresh groundwater and seawater. The multi-isotope approach consisting of complementary tracers allows evidencing water-rock interaction processes, such as dissolution or adsorption onto clay matrices.

Keywords: salinization; water-rock interaction; cation exhange; isotopes; Roussillon Basin.

1. Introduction

The sedimentary aquifer of the Roussillon Basin, close to the Mediterranean Sea (southern France) is a perfect example of a geometric and hydrogeological complexity facing seasonally salinization problem and increase of water abstraction. These coastal aquifers thus constitute fragile environments due to potential seawater intrusions. Classical methods of investigation consist in punctual measurements of salinity that only allow identifying local marine intrusions.

The ANR "GRAIN D'SEL" project aims at developing and validating new approaches to improve the knowledge and the monitoring of coastal detrital aquifers at different scales (regional up to local with borehole monitoring observatories). The combined use of various approaches (geophysics at various

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scales, including airborne electromagnetism, hydro-geophysics and hydro-geochemistry including isotopes) is a real innovation in integrated instrumentation system: their confrontation and integration can bring elements to better understand both the complex geometry of these aquifers and their hydrodynamic, on a test site in the Roussillon Basin. The final objective being to develop a monitoring and warning system of saline intrusion, based on a 3D hydrodynamic modeling including density effect, at a local scale and under non-steady state.

Part of this study consists in a multi-isotopic fingerprinting approach of the water system, including $\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{34}S\text{-}SO_4$, $\delta^{18}O\text{-}SO_4$. In addition to chemical parameters (Cl, Br, B, SO_4, major and trace cations), isotopic tracers will help to better constrain water circulations (recharge, leakage between the aquifer layers), and to elucidate the impacts of salinization on chemical composition. Each isotopic systematic has its own properties and abilities to trace the origin of water and of the associated dissolved elements, to identify water-rock interaction (e.g. adsorption/desorption), geochemical processes in the aquifer (e.g. dissolution, bacterial reduction, evaporation), and also to quantify mixing of waters from different origin. This combination of environmental isotopic tracers will provide strong constraints on the functioning of the Plio-Quaternary coastal aquifer system in the Roussillon Basin.

2. Geological and Hydrogeological settings

The Roussillon sedimentary basin (fig.1) is composed of Pliocene sediments and Quaternary deposits due to the interglacial transgression and regression phases. The last transgression resulted in a lagoon area from Leucate to Argelès, only the Salses-Leucate and Canet lagoons are still present.

The Roussillon Basin is characterized by the presence of a quaternary geological unit composed of Pleistocene riverine terraces and modern Holocene deposits, lying on two geological units named Continental Pliocene and Marine Pliocene respectively [1]. This Plio-Quaternary unit is in discordance on various Miocene formations and synchronous to the formation of the Roussillon rift basin.

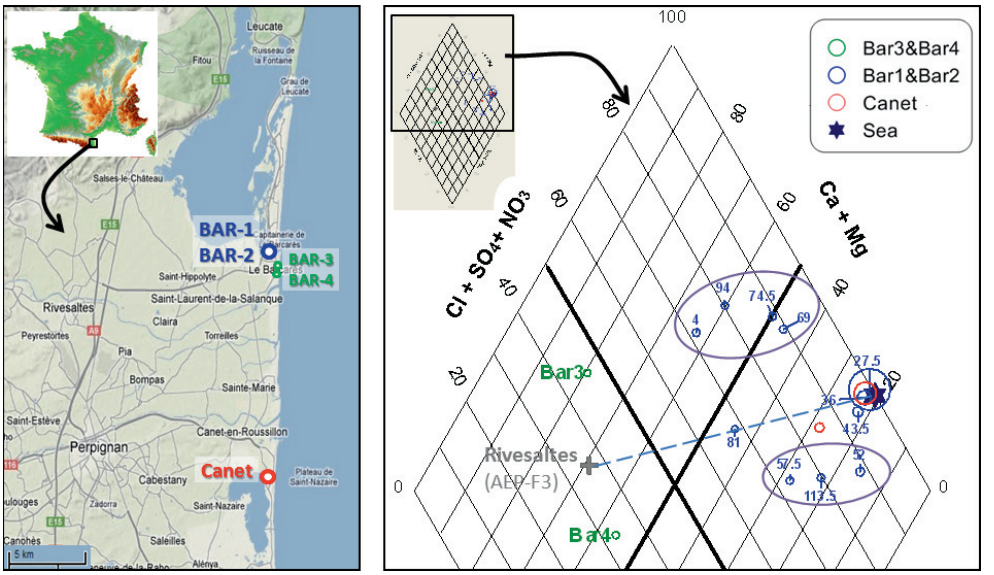

Fig. 1. (a) Study site and sampling location in the Roussillon Basin; (b) Part of the diamond of the Piper diagram showing water type according to water-rock interactions and adsorption-desorption processes.

Each aquifer layer includes several aquifer compartments characterized by different hydrogeological properties. Aquifers are grouped according to the following hydrogeological entities:

The Pliocene aquifer is composed of marine and fluvial sands which constitute the two main Pliocene aquifers: (1) the Continental Pliocene aquifer presents highly mineralized water mainly in the northern part of the basin, along the lagoon and even more along the coast at Barcarès; (2) the Marine Pliocene aquifer is composed of sandy marine sediments, theoretically not connected to the sea and thus preserved from seawater intrusion. However, part of this aquifer is highly mineralized, probably because of vertical leakage from the partially contaminated Quaternary aquifers to the Pliocene ones. This can be due to the existence of improperly constructed wells as new boreholes drilled next to the old ones show a strong decrease in the salt content [2]. Finally, a non-continuous impervious layer separates the Continental Pliocene aquifer from the sandy Marine Pliocene aquifer. This aquaclude is mainly composed of lignite layers alternating with plastic marsh clays found at the bottom of the Continental Pliocene aquifer.

The Quaternary aquifer is mainly composed of alluvium (conglomerates) and coastal deposits. The unconfined Quaternary aquifer lies along the main rivers and the coastline. The water quality of the Quaternary upper aquifer is poor near the coast due to a high chloride concentration.

3. Chemical and isotopic investigations

Two test sites were selected in the Roussillon Basin, both for hydro-geophysics monitoring and chemical and isotopic approach in order to characterize the saline intrusion at the coastal dune and underlying formations. The Barcarès site aims to characterize the freshwater / saltwater interface within the Continental Pliocene aquifer and the Marine sandy Pliocene aquifer, as well as the physical properties and geometry of the prisms. The Canet site aims to characterize the freshwater / saltwater interface in the Quaternary aquifer along the coast (Fig.1).

In Barcarès (wells Bar1 and Bar2), samples were taken at 11 different depths between 4 and 113.5 m in wells equipped with Westbay systems. Two samples were taken in the Canet well, using the same procedure. Two historical monitoring wells were also sampled along the beach at Barcarès (Bar3 and Bar4), screens being placed at different levels in the Pliocene aquifer. Finally, local seawater was also sampled during this high flow period (May 2012). Physico-chemical parameters were measured in situ and chemical and isotopic analyses were performed in BRGM Labs using HPLC, ICP-AES, ICP-MS, TIMS and CF-IRMS technics.

The Electric Conductivity (EC, Fig. 2; reflecting the total mineralization of water) presents large variations between 459 (Bar4) and 43 000 $\mu S.cm^{-1}$ (Bar1-27.5m). Variations within the same well at various depths are also significant, from 926 up to 43 000 $\mu S.cm^{-1}$ in the Barcarès well, at 81m and 27.5m respectively; the highest mineralization corresponding to about 80% of that of the local seawater. Groundwater shows mostly a sodium chlorine type (Fig.1), with some samples very close to the seawater, another group shows a calcium chlorine type, whereas historical monitoring wells (Bar3, Bar4) present a calcium bicarbonate facies. A deep Pliocene reference sample (far from any marine influence) from the western part of the Roussillon Basin (Rivesaltes, [3]) is also reported. A simple conservative binary mixing between fresh water (Rivesaltes) and seawater would give samples plotting on a straight line between these two end-members (Fig.1)[4]. Samples above this line presenting a Ca excess, compared to conservative mixing, can be related to seawater intrusion with cation exchange, while samples below this line, with a Na excess may indicate freshening of the aquifer, also accompanied by cation exchange. These phenomena can be further investigated using trace elements and various isotopic tools.

In a δ^2H vs. $\delta^{18}O$ diagram (not shown), most of the groundwater samples plot along the global meteoric water line with signatures consistent with a recharge coming from the western part of the basin. Some samples present enriched values and plot along a mixing line between the recharge and seawater,

confirming seawater intrusion at different depths in the Pliocene aquifer. Strontium isotopes are considered as ideal tracers of water-rock interaction. The vertical profile of $^{87}Sr/^{86}Sr$ in the Barcarès well presents high variation from 0.70885 to 0.71083 (Fig. 2). Up to 60m, the $^{87}Sr/^{86}Sr$ is close to the seawater ratio and then the isotopic ratio increases with depth, reflecting water-rock interaction with argillaceous formations. Two points present values lower than seawater implying the contribution of a reservoir with low $^{87}Sr/^{86}Sr$. Boron isotopes are susceptible to fractionate by adsorption on clays especially in high saline conditions [5] and thus can trace secondary processes such as adsorption/desorption processes involved by salinization. The vertical profile of $\delta^{11}B$ in the Barcarès well presents high variation from 20.3‰ to 45.4‰ (Fig. 2), with several levels of the Pliocene aquifer presenting a signature higher than that of seawater, suggesting isotopic fractionation due to preferential adsorption of ^{10}B onto clays.

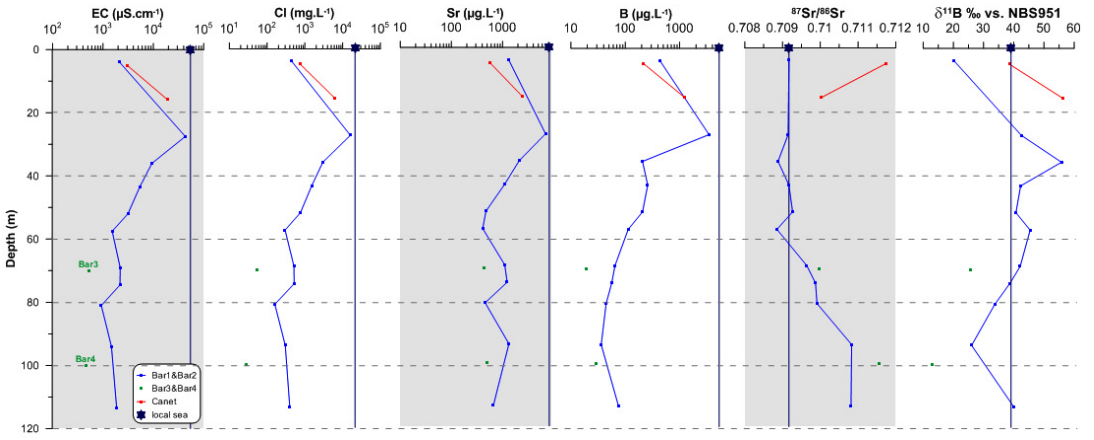

Fig. 2. Vertical profiles of Barcarès and Canet wells. Electric Conductivity (EC), Chloride, Strontium and Boron content (log scales) together with Sr and B isotopic compositions. Local seawater values are reported for comparison.

This work illustrates the complexity of this aquifer system and the processes induced by salinization, and it points out the capability of multi-isotopes tracing to further constrain both origin of the elements and salinity as well as secondary processes.

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